



TITLE:

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CITATION:

Osugi, Jiro ...[et al]. Kinetic studies on fast reactions in solution III : photoreduction of anthracene derivatives. The Review of Physical Chemistry of Japan 1967, 37(2): 94-104

ISSUE DATE:

1967

URL:

<http://hdl.handle.net/2433/46903>

RIGHT:

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 37, No. 2, 1967

KINETIC STUDIES ON FAST REACTIONS IN SOLUTION III

Photoreduction of Anthracene Derivatives

BY JIRO OSUGI, SIGERU KUSUHARA AND SATOSHI HIRAYAMA

The photoreduction of 9-acetylanthracene by stannane in benzene was studied. By the analysis of UV and IR spectra of the reaction products, it was found that the carbonyl group of 9-acetylanthracene was not photoreduced, and that the addition of hydrogen atom occurred at the meso position.

For several anthracene derivatives, this photoreduction reaction at the meso positions was investigated by the method of the flash photolysis. The reduction rate constants are of the order of $10^4 \text{ l mole}^{-1} \text{ sec}^{-1}$. The trend of the substituent effect is reverse to that found by other investigators for the photo-oxidation of anthracene derivatives. Namely, the electron donating substituents decrease the rate of the photoreduction and the electron attracting substituents increase it.

The activation energy for the reaction of 9-acetylanthracene was found to be 10.4 kcal/mole.

The reason why the carbonyl group of 9-acetylanthracene was not photoreduced by stannane will be discussed.

Introduction

In the previous paper¹⁾ we have reported the kinetical results of the photoreduction of 2-acetonaphthone with stannane investigated by the flash photolysis. As stated there, it would be quite interesting to study the effects of the differences in the excited states (*e.g.* $\pi \pi^*$, $n \pi^*$, CT, etc.) or of the excited state energies of aromatic ketones on the photoreduction.

From this view, we made the same experiments with 9-acetylanthracene as with 2-acetonaphthone, where the former is considered to have the triplet state ($\pi \pi^*$) of lower energy than the latter²⁾.

By the analysis of UV and IR spectra of the reaction products, it was found that the carbonyl group of 9-acetylanthracene was not photoreduced, and that the addition of hydrogen atom occurred at the meso position. This result is contrary to that of 2-acetonaphthone, whose carbonyl group is easily photoreduced by stannane.

As far as we know, the photoreduction reactions of anthracene and its derivatives have not yet been studied quantitatively except for the qualitative study by Norrish *et al.*³⁾, who used cumene as the reducing agent. Therefore we think it is valuable to study the photoreduction reaction of the anthracene and its derivatives as well as to consider the reason why the carbonyl group of 9-acetylanthracene

(Received January 15, 1968)

- 1) J. Osugi, S. Kusuhara and S. Hirayama, *This Journal*, **36**, 93 (1966)
- 2) Compared with 2-acetonaphthone, 9-acetylanthracene has a larger conjugated system and so its lowest triplet ($\pi\pi^*$) state energy is considered to be lower than that of the former. About its value see the foot note 23).
- 3) R. G. W. Norrish and J. P. Simons, *Proc. Roy. Soc., A* **251**, 4 (1959)

was not photoreduced by stannane.

Anthracene derivatives are very interesting substances in photochemistry and not only their physical properties concerned with light but also their photochemical reactions such as photodimerization^{4)~7)}, photo-oxidation^{8)~11)}, reaction with solvents¹¹⁾¹²⁾ and co-polymerization³⁾, have been studied in detail. In these reactions the nature of the reactive excited states and the substituent effects have mainly been discussed. Because of the nature of these reactions, there is no better way than to measure their quantum yields for the kinetical study of them. These values, however, depend on several other factors, such as the stability of the intermediate products (e.g. Fig. 2 I), the quantum yield of the production of the reactive excited state, etc. which have no direct connections with the elementary processes, so it becomes difficult to get the direct informations on the elementary processes.

But in the case of the photoreduction of the anthracene derivatives reported in this paper, the reduction rate constants of their triplet states can be obtained directly by the method of the flash photolysis.

The photoreduction rate constants of the anthracene derivatives (9-methyl-, 9-chloro-, 9-acetyl-, 9-(α -hydroxyethyl)-, 9-phenyl-, anthracene derivatives and anthracene) and its activation energy for 9-acetylanthracene will be reported, and the substituent effects of the photoreduction will be compared with those of photo-oxidation by Vember *et al.*⁸⁾ and Bowen *et al.*¹¹⁾ and with those of the reaction with the solvent (CCl₄) by Bowen *et al.*¹¹⁾. The reason why the carbonyl group of 9-acetylanthracene was not photoreduced by stannane will be discussed based on the concept of Suppan.

Experimentals

Apparatus

The details of the apparatus of the flash photolysis used to measure the photoreduction rate constants have been described in the previous paper¹⁾.

Material

Anthracene of the scintillation grade was used. 9-Methyl¹³⁾, 9-chloro¹⁴⁾, 9-acetyl¹⁵⁾, 9-(α -hydroxyethyl¹⁶⁾, anthracene derivatives were synthesized according to the methods described in the litera-

- 4) Frederick D. Greene, S. Leslie Misrock and James R. Wolfe, Jr., *J. Am. Chem. Soc.*, **77**, 3852 (1955)
- 5) A. Mustafa, *Chem. Rev.*, **51**, 1 (1952)
- 6) M. Suzuki, *Bull. Chem. Soc. Japan*, **22**, 172 (1949)
- 7) M. Suzuki, *ibid.*, **23**, 120 (1950)
- 8) T. M. Vember, L. A. Kiyanskaya, A. S. Cherkasov, *J. Gen. Chem. USSR (English Transl.)*, **53**, 2281 (1963)
- 9) G. O. Schenck, *Naturwiss.*, **41**, 452 (1954)
- 10) E. J. Bowen and D. W. Tanner, *Trans. Faraday Soc.*, **51**, 475 (1955)
- 11) E. J. Bowen and K. K. Rohatgi, *Discussions Faraday Soc.*, **14**, 146 (1953)
- 12) S. Kusuha and R. Hardwick, *J. Chem. Phys.*, **41**, 2386 (1964)
- 13) A. L. J. Beckwith and A. Waters, *J. Chem. Soc.*, **1956**, 1108
- 14) D. E. Applequist, E. C. Friedrich and M. T. Rogers, *J. Am. Chem. Soc.*, **81**, 457 (1959)
- 15) E. G. E. Hawkins, *J. Chem. Soc.*, **1957**, 3858
- 16) E. L. May and E. Mosetting, *J. Am. Chem. Soc.*, **73**, 1301 (1951)

tures and recrystallized several times from the appropriate solvents. 9-Phenylanthracene¹⁷⁾ was purified by the thin layer chromatography after synthesis. The reducing agent Bu_3SnH was synthesized as stated in the previous paper. The spectro-grade benzene was used as the solvent and the samples were degassed by repeating a freeze-pump-thaw cycle six times. The measurements were made at the concentrations $3 \times 10^{-5} \sim 5 \times 10^{-5}$ mole/l for the anthracene derivatives and 2×10^{-1} mole/l for stannane.

UV absorption spectra

The UV absorption spectra of the reaction products and the reactants were measured with Perkin-Elmer Model 202 spectrophotometer. The results are shown in Fig. 1. The solid line was obtained for 9-acetylanthracene (*ca.* 3×10^{-5} mole/l) before outgassing in the presence of stannane (2×10^{-1} mole/l)¹⁸⁾. (Below $300\text{m}\mu$ it was extrapolated by the UV absorption spectrum measured in cyclohexane.) The absorption in the range of $320\text{m}\mu \sim 400\text{m}\mu$ is due to the p-band of the anthracene ring. The broken line is for the reaction products which were obtained by exposing the degassed sample (9-acetyl-

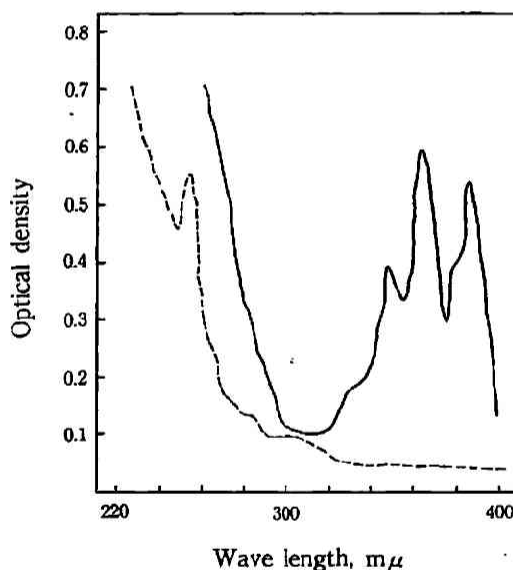


Fig. 1 UV absorption spectra

- The absorption spectrum of 9-acetylanthracene ($9\text{-acetylanthracene } 3 \times 10^{-5}\text{mole/l, stannane } 2 \times 10^{-1}\text{mole/l}$) before the reaction
 - The reaction products ($9\text{-acetylanthracene } 5 \times 10^{-5}\text{mole/l, stannane } 10^{-4}\text{mole/l}$)
- For further details, see the text.

17) P. L. Julian, W. Cole, G. Piemer and J. G. Schafer, *J. Am. Chem. Soc.*, **71**, 2058 (1949)

18) When the sample of these concentrations is degassed and exposed to the sun, in 30 to 60 minutes the p-band disappears. But when not degassed, the absorption spectrum hardly changes. It shows that it is the reaction in the triplet state. Anthracene was also observed to react with stannane when the solution was irradiated with the medium pressure mercury lamp at $366\text{m}\mu$.

anthracene 5×10^{-5} mole/l and stannane 10^{-4} mole/l in benzene) to the sun for a week¹⁹⁾, evaporating out benzene under vacuum and dissolving the residue in the appropriate amount of cyclohexane. The p-band also disappears when photodimerization or photo-oxidation occurs, but in the outgassed and dilute solutions, both of them can safely be neglected. This is clearly shown by the fact that in the absence of stannane the spectrum of 9-acetylanthracene hardly changes by exposing its benzene-solution to the sun for several days.

The concentration of stannane was chosen as it was about twice as high as that of 9-acetylanthracene from the following reasons. If stannane is far in excess as in the experiments by the flash photolysis, it becomes difficult to observe the absorption below $280\text{m}\mu$ owing to the tail of stannane itself which has its absorption maximum about $220\text{m}\mu$. (It is not easy to remove stannane alone after the reaction.) Furthermore stannane will be used up mainly by either the carbonyl group or the meso positions of 9-acetylanthracene which are more feasibly reduced, and will produce dominantly either the product II or the products producible from I ($\text{R}=\text{CH}_3\text{CO}$) in Fig. 2. So whether the p-band exists or disappears in the products can tell the more reactive site of the two.

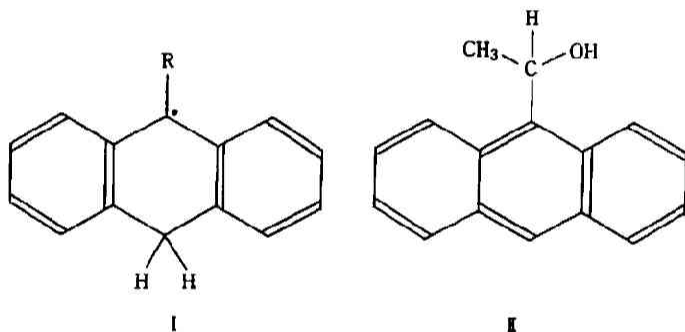


Fig. 2. Plausible products of the photoreduction
(R=H, CH₃, Cl, C₆H₅, CH₃CO, CH₃CHOH)

The absorption spectrum of the products which is shown by the broken line in Fig. 1 does not indicate the existence of the p-band. It resembles the absorption spectra of 9, 10 substituted dihydroanthracene^{20,21}. From these facts the additions are considered to have occurred at the meso positions of 9-acetylanthracene in the reaction with stannane. The disappearance of the p-band was observed on all the anthracene derivatives studied here.

IR absorption spectra

The IR absorption spectra of 9-acetylanthracene, 9-(α -hydroxyethyl)-anthracene, stannane and the reaction products (see the note at the bottom of Table 1) were recorded on Japan Spectroscopic Co., Ltd. Model DS-402G infrared spectrophotometer.

Only the positions of the absorption maxima necessary for the following discussion are listed in

19) It was exposed to the sun for a week because the concentration of stannane was two-thousandths of that of stannane used in the experiments by the flash photolysis.

20) D. D. Phillips and J. Cason, *J. Am. Chem. Soc.*, **74**, 2934 (1952)

21) M. Metayer, *Bull. Soc. Chim. France*, 1954, 614

Table 1 IR absorption spectra

Atomic group	O—H cm ⁻¹	C=O cm ⁻¹	Sn—H cm ⁻¹
Substance			
9-acetylanthracene	—	1695	—
9-(α -hydroxyethyl)-anthracene	3590	—	—
stannane	—	—	1820
products a)	not observed	1695 1705	very weak

a) The products were obtained by exposing the degassed sample (9-acetylanthracene *ca.* 6×10^{-3} mole/l and stannane *ca.* 6×10^{-3} mole/l in benzene) to the sun for a week, evaporating out benzene under vacuum, and dissolving the residue in a bit of CCl₄.

Table 1. 9-(α -Hydroxyethyl)-anthracene, which is expected to be produced if the carbonyl group of 9-acetylanthracene is photoreduced, has the strong absorption maximum of O—H group at 3950 cm⁻¹. (9-(α -Hydroxyethyl)-anthracene was synthesized by the reduction of 9-acetylanthracene with LiAlH₄.) No absorption of O—H group was, however, observed in the products. Therefore, it is concluded that the carbonyl group of 9-acetylanthracene can not be photoreduced to such an extent as to be detectable by IR absorption spectra. Moreover in the products, the absorption maximum of the carbonyl group was detected to be shifted to the shorter wave length to some extent. This is because the carbonyl group, which had been conjugated with the anthracene ring, was isolated on account of the additions at the meso positions. It is well known that the positions of the absorption maxima of the free carbonyl groups shift to the shorter wave length than those of the conjugated carbonyl groups. The absorption of Sn—H became very weak.

All these things indicate that the addition of hydrogen atoms has occurred at the meso positions. The final products, however, will be quite complicated as was found for the reaction of anthracene with carbon tetrachloride¹¹⁾ and will be composed of several derivatives of 9, 10-dihydroanthracene. In fact the products gave six spots at least by the thin layer chromatography, but the identification of the final products was not made.

Kinetical treatments

From the results of UV and IR spectra stated above it is safely concluded that the carbonyl group of 9-acetylanthracene is not photoreduced by stannane and that the addition of hydrogen atoms occurs at the meso positions of the anthracene ring. The rate constants of six anthracene derivatives for the reaction of their triplet states with stannane were determined as follows.

The general rate equation of the decay of the triplet molecules is,

$$-\frac{d[A_3^*]}{dt} = k_1[A_3^*] + k_2[A_3^*][DH] + k_3[A_3^*]^2 \quad (1)$$

- where A_3^* : molecules in the lowest triplet state
 k_1 : the pseudo first order decay rate constant of the molecules in the lowest triplet state
 k_2 : the rate constant of triplet-triplet annihilation
 k_r : the reduction rate constant
 DH: the reducing agent

In general the third term in equation (1) can not be neglected, but when $[A_3^*]$ is very small it can be neglected, and as the approximation²²⁾ equation (1) can be rewritten.

$$\frac{d[A_3^*]}{dt} = -(k_1 + k_r[DH])[A_3^*]. \quad (2)$$

The concentration of stannane is so high that there is a possibility that a process other than the reduction process occurs and the decay rate of the triplet state becomes large. To make this effect clear we used the same amount of Bu_4Sn which has no reducing ability instead of stannane and were assured that Bu_4Sn had no effect on the decay rate. So that the increase of the decay rate on the addition of stannane can be ascribed purely to the appearance of the reducing processes as was found in the case of 2-acetonaphthone. The absorption of the radical (Fig. 1 I) which is probably the intermediate product

Table 2 Rate constants and quantum yields

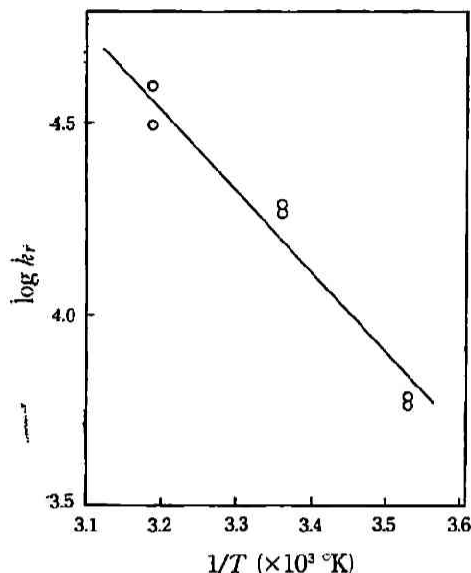
Substance	T-T' absorption ^{a)} (m μ)	Reduction rate-constant ^{b)} ($\times 10^{-3}$) l mole ⁻¹ sec ⁻¹	Quantum yield of photo oxidation c) d)		Quantum yield of reaction with CCl_4 ^{e)}
9-acetylanthracene	425	19	—	0.00	—
9-chloroanthracene	427	10	0.63	0.006	0.18
9-phenylanthracene	438	4.8	0.85	0.003	0.156
anthracene	430	13	0.75	0.010	0.4
9-(α -hydroxyethyl)-anthracene	435	4.8	—	0.012	—
9-methylantracene	432	8.8	1.3	0.046	0.2

- a) The life times of the transients which show absorptions listed in Table 2 are of the order of several hundred μ sec and the absorption maxima are very close to that of T-T' absorption of anthracene²⁴⁾. So these absorptions in Table 2 are considered to be those of triplet states. The values are in benzene solutions.
 b) At 25°C and stannane 2×10^{-1} mole/l
 c) The quantum yields of photo-oxidation depend on the initial concentration of the anthracene derivatives. Reference 11)
 d) Reference 8)

22) In order to approximate equation (1) by equation (2), the later part of the triplet decay curve was used for calculation. If we admit the experimental error of flash photolysis is about 10%, it will not cause much error to neglect the third term. The more exact equation (1), whose treatment has been stated by Linschitz *et al.*²³⁾ was not used on account of its intricacy.

23) H. Linschitz and K. Sarkanen, *J. Am. Chem. Soc.*, **80**, 4826 (1958)

24) G. Porter and M. W. Windsor, *Proc. Roy. Soc., A* **245**, 238 (1958)

Fig. 3 Arrhenius plot of k_r

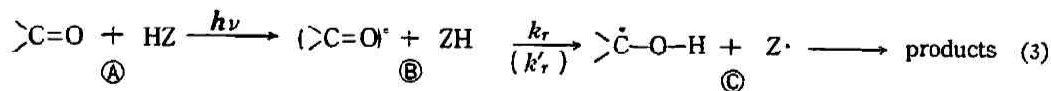
of the photoreduction was not observed in the range of $400\text{ m}\mu\sim 600\text{ m}\mu$. The measurement below $400\text{ m}\mu$ could not be made because of the absorption of the anthracene derivatives themselves.

k_r 's which were obtained by using equation (2), the wave lengths of T-T' absorption where the measurements were made, the quantum yields of photo-oxidation of anthracene derivatives by Vember *et al.* and those by Bowen *et al.* and the quantum yields of the reaction with CCl_4 by Bowen *et al.* are listed in Table 2.

Fig. 3 shows the temperature dependence of k_r for 9-acetylanthracene. By the method of the least squares we obtained 10.4 kcal/mole as the activation energy, and $10^{11.8}$ as the preexponential factor. The discussion about these will be made in the later part of this paper.

Discussion

The reason why the carbonyl group of 9-acetylanthracene was not photoreduced by stannane: Recently Suppan²⁵⁾ has stated a very interesting idea as to the photoreduction of the aromatic ketones. According to him, the photoreduction of aromatic ketones is generally represented as follows,



He considers that the excited molecules are the new ones in thermal equilibrium with the system and that the photoreduction rate constant can be represented by the Arrhenius equation,

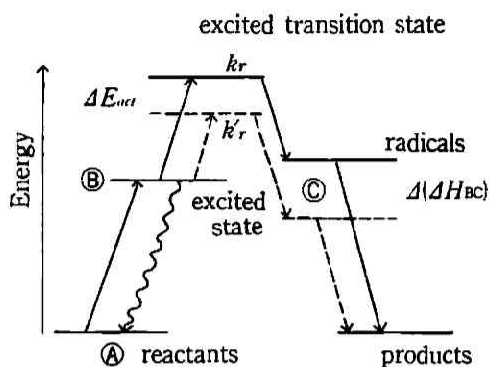


Fig. 4 Schematic energy diagram of the photoreduction system
The energy difference between ① and products is immaterial in the discussion here. About ①, ② and ③ see equation(3).

25) P. Suppan, "The Chemistry of Ionization and Excitation", p. 103, ed. by G.R.A. Jonson and G. Scholes, Taylor and Francis Ltd. (1967)

$$k_r = A \exp\{-(E_a + E_L^*)/RT\}, \quad (4)$$

where $(E_a + E_L^*)$ is the activation energy. The greater part of E_a is the electrostatic energy between the carbonyl group and the reducing agent. (The electron distribution is considered to be $>C^{\delta+}=O^{\delta-} \leftarrow {}^{\delta-}H-Z$). E_L^* is called "antibonding localization energy" and is the energy necessary to localize an electron in the antibonding orbital of the carbonyl group. In the $(n \pi^*)$ triplet state this energy is zero but in the $(\pi \pi^*)$ state it takes some positive value and largely contributes to the activation energy. Using alcohol as the reducing agent good agreements with the experiments have been obtained. But in equation (4), the change in the activation energy accompanying the variation of the bond energy of the reducing agent HZ is not taken into account. To consider this change we modify equation (4).

The enthalpy change ΔH_{AC} of the process (A) to (C) in equation (3) is approximately (the bond energy of the π -bond of the carbonyl group) + (the bond energy of HZ) - (the bond energy of O-H of the ketyl radical produced). When the reducing agent is changed, ΔH_{AC} will change by the amount of the difference in the bond energies of the reducing agents. The enthalpy change ΔH_{BC} of the process (B) to (C) will also change by the same amount.

Now we use the relation between the change in the enthalpy of the reaction $\Delta(\Delta H)$ and that in the activation energy ΔE_{act} (the relation proposed by Evans and Polanyi²⁶⁾). Considering that the change in $\Delta(\Delta H)$ is equal to the difference in the bond energies of the two reducing agents, equation (5) follows,

$$\Delta(\Delta H_{BC}) = \Delta E_{bond}, \quad \Delta E_{act} = \alpha \Delta(\Delta H_{BC}), \quad (5)$$

where α is the positive proportional constant.

As an example, two different reducing agents, alcohol and stannane, are taken. Then,

$$\begin{aligned} \Delta(\Delta H_{BC}) &= E_{C-H} - E_{Sn-H} \\ \Delta E_{act} &= \alpha(E_{C-H} - E_{Sn-H}), \end{aligned} \quad (6)$$

where E_{C-H} , E_{Sn-H} represent the bond energies of C-H and Sn-H, respectively.

So, when stannane is used as the reducing agent, from equations (4) and (6) k_r will be rewritten as²⁷⁾,

$$k_r = A' \exp\{ -[(E_a + E_L^*) - \alpha(E_{C-H} - E_{Sn-H})]/RT \}. \quad (7)$$

All these circumstances are shown schematically in Fig. 3.

Next using equation (7) we will show that 9-acetylanthracene was not photoreduced by stannane. Designating the photoreduction rate constants for the carbonyl groups of 2-acetonaphthone and 9-acetylanthracene as k_{r1} and k_{r2} , respectively, equation (8) is obtained from equation (7).

$$\frac{k_{r2}}{k_{r1}} = \frac{A_2 \exp\{ -[(E_{a2} + E_{L2}^*) - \alpha_2(E_{C-H} - E_{Sn-H})]/RT \}}{A_1 \exp\{ -[(E_{a1} + E_{L1}^*) - \alpha_1(E_{C-H} - E_{Sn-H})]/RT \}} \quad (8)$$

26) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1934)

27) If we assume $1/3 \sim 1/4$ to α and ~ 30 kcal/mole to $E_{C-H} - E_{Sn-H}$, we obtain the value of the order of 1.7 kcal/mole which is the activation energy of 2-acetonaphthone. But α will be different for the different pair of the reducing agents.

In this case, the structures of the reactants, 2-acetonaphthone and 9-acetylanthracene, are quite similar, so that A_1 and A_2 can be considered to be the same without much error. E_{a_1} and E_{a_2} are the electrostatic energies between the reducing agent and the substances to be reduced in the $(\pi \pi^*)$ state, and are small (ca. 4 kcal/mole) compared with $E_{L_1}^* - E_{L_2}^*$, so we regard them as equal. Furthermore to make equation (8) simpler, we put α_1 and α_2 equal. All these approximations are not so bad if we consider the similarity of the reactions and the qualitative character of the discussion. Then equation (8) becomes much simpler as follows,

$$\frac{k_{r_2}}{k_{r_1}} = \exp\{-(E_{L_2}^* - E_{L_1}^*)/RT\}. \quad (9)$$

The $(n \pi^*)$ triplet state energy, as is generally recognized, does not vary to a great degree with the conjugation and we assume the same value $E_{(n \pi^*)}$ for the two substances. Then by the definition,

$$\begin{aligned} E_{L_1}^* &= E_{(n \pi^*)} - E_{1(\pi \pi^*)} \\ E_{L_2}^* &= E_{(n \pi^*)} - E_{2(\pi \pi^*)}, \end{aligned} \quad (10)$$

where $E_{1(\pi \pi^*)}$, $E_{2(\pi \pi^*)}$ are the lowest triplet state energies for the corresponding substances.

If 60 kcal/mole and 40 kcal/mole²⁸⁾ are used for them, respectively, equation (11) is obtained from equations (9) and (10).

$$\frac{k_{r_2}}{k_{r_1}} = \exp(E_{2(\pi \pi^*)} - E_{1(\pi \pi^*)})/RT = \exp(-2 \times 10^4/RT) \simeq 10^{-14} \quad (11)$$

Therefore we can conclude that the carbonyl group of 9-acetylanthracene can not react with stanane. Equation (11) generally indicates that in the aromatic ketones, if their lowest triplet states are of $(\pi \pi^*)$ character, the reactivity of their carbonyl groups to the photoreduction will decrease as their energy levels become lower. The low reactivity of the carbonyl group of 9-acetylanthracene is explained also in terms of the character of its excited state. When the energy of the triplet $(\pi \pi^*)$ state becomes much lower than that of the $(n \pi^*)$ state, the character of the excited state becomes dissimilar to the $(n \pi^*)$ state of high reactivity to the photoreduction and is determined almost by the aromatic compounds²⁹⁾ (e.g. anthracene and naphthalene) which compose aromatic ketones. Therefore the lower the triplet state energy $(\pi \pi^*)$ becomes, the lower the reactivity of the carbonyl group becomes.

But it must not be forgotten that in order to get equation (11) many assumptions and approximations are made, so that equation (11) has nothing but qualitative meaning and that its application is limited to the similar reactions involving the aromatic ketones of the same kind.

Activation energy: 10.4 kcal/mole was obtained for 9-acetylanthracene as the activation energy of its photoreduction. This value is, as stated before, not for the reduction of the carbonyl group but for the reduction of the meso position of 9-acetylanthracene. As the activation energy for the reaction of this kind has not been measured so far, we can not say much about the validity of its value. It must be considered, however, that the range of temperature is narrow because of the low boiling point and the high freezing point of benzene used as the solvent and that this causes some error to the acti-

28) The energy of the lowest triplet state of 9-acetylanthracene is assumed to be close to that of anthracene (42 kcal/mole) and taken to be 40 kcal/mole.

29) D. S. McClure, *J. Chem. Phys.*, **8**, 905 (1949)

vation energy and that the steric hindrance of the three rather bulky butyl groups of stannane makes the preexponential factor small. Therefore, it might be appropriate to consider a little smaller activation energy.

It is necessary for the data concerning these to be accumulated.

Substituent effect: In the photochemical reactions, the quantum yields obtained from the amount of the decrease of the reactants or from the amount of the formation of products can not be a measure of the reactivity of the elementary processes, because they depend on the efficiency of the excited state formation (e.g. the intersystem crossing efficiency), the stability of intermediate products, the reaction mechanisms and so on³⁰⁾.

On that account the direct comparison of k_r 's with the quantum yields listed in Table 2 can not be made without much caution. But according to the authors³⁰⁾ in the case of the photo-oxidation the electron donating substituents, such as alkyl group and methoxy group favour the reaction. On the other hand, the electron attracting substituents retard or completely prohibit the reaction. In the 9, 10-disubstituted derivatives the effect is strengthened. It is caused by the changes in the electron densities at the meso positions where oxygen molecule attacks. In the case of the reactions with carbon tetrachloride the effect of the substituents is not so conspicuous as in the photo-oxidation.

Comparing our results with those of the photo-oxidation, it is the most remarkable thing that 9-acetylanthracene which is not photo-oxidized is photoreduced most easily. In addition, although it is difficult to relate them quantitatively, the electron accepting substituents, such as the acetyl group and the chlorine atom, seem to favour the reaction compared with the electron donating substituents such as methyl group. Namely, the substituent effect is reverse to that of the photo-oxidation. This is explained by the electron distribution of stannane $\text{Sn}^{+\delta}-\text{H}^{-\delta}$ implied by the electronegativities and compatible with the substituent effect found for the intramolecular hydrogen abstraction reactions of the butyrophenone derivatives³¹⁾.

9-Phenylanthracene, which seems to be more easily photoreduced from the datum of the photo-oxidation by Vember *et al.*³²⁾, in Table 2, is photoreduced less easily. Is this because the phenyl group acts as the electron accepting group? It must be considered with much care. The low quantum yield of the photo-oxidation of 9-phenylanthracene can not be ascribed only to the low reactivity because its intersystem crossing efficiency is very low³⁰⁾. In fact 9, 10-diphenylanthracene is more readily photo-oxidized in spite of its lower intersystem crossing efficiency than 9-phenylanthracene.

Taking account of these facts, we consider that the phenyl group acts as an electron donating

30) If the photo-oxidation of the anthracene derivatives occurs in the triplet, as is generally recognized, the quantum yields depend on the intersystem crossing efficiency. In the case of 9-phenylanthracene the quantum yield of fluorescence is very large compared with other anthracene derivatives and on that account its quantum yield of triplet formation becomes low. Therefore we can not conclude immediately that 9-phenylanthracene has low reactivity to the photo-oxidation.

31) E. J. Baum, J. K. S. Wan and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **88**, 2652 (1966)

32) The data by Bowen *et al.* show that it is more reactive than anthracene, but Vember *et al.* considered the substituent effects, making a wide variety of experiments, so we use the datum of 9-phenylanthracene by the latter.

group (it is not sure to what extent it does because the phenyl group is not coplanar with the anthracene ring) and retard the photoreduction rate.

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